



Al₂O₃/SiC NANOCOMPOSITE ABRASIVE GRAINS, METHOD FOR PRODUCING THEM AND THEIR USE

Description

Field of the Invention

~~Al₂O₃/SiC nanocomposite abrasive grains, a method for their production, and their use.~~

[0001] The present invention at hand concerns in one aspect sintered Al₂O₃/SiC nanocomposite abrasive grains having hardness greater than 16 GPa, densities greater than 95% of the theoretical limit, and an SiC portion of between 0.1 and < 5 mol %, relative to the Al₂O₃ matrix, wherein the SiC particles are present in the Al₂O₃ matrix as well as intra-granularly and the abrasive grain shows a performance factor LF₂₅ > 75 % in the single-grain scratch test, and ~~in accordance with the characterizing clause of Claim 11; a process for their production in accordance with the characterizing clause of Claim 1; as well as their use as abrasives.~~

Background of the Invention

[0002] Abrasive grains on Al₂O₃ basis are processed industrially in large quantities into abrasives due to their great hardness, chemical inertness and high temperature resistance. In addition to melting corundum that can be produced relatively cost-effectively in the arc furnace, sinter corundums obtained via a ceramic or chemical route have been used more extensively in recent times for certain areas of application. The advantage of sinter corundums, in terms of abrasive engineering, is based on their microcrystalline structure which in turn leads to a particular wear mechanism of the abrasive grain during the grinding process. Especially in applications that require high pressures [against the work piece] such as, e.g., the processing of special steels, hardened steels or hard-to-chip alloys, the abrasion output can be markedly increased through the use of sinter corundums. The sinter corundum with its microcrystalline structure is considerably more wear resistant for those applications than the melting corundum with its macro-crystalline structure. In addition, during the grinding with microcrystalline corundums, small segments break off, forming new cutting edges that in turn intervene in the grinding process. Such a self-sharpening of the grain does not take place in the case of macro-

crystalline melting corundums because the cracks that are caused by the mechanical stress of the grain can no longer be deflected, but rather proceed through the entire grain along the crystal plane surface through the entire grain, thereby leading to the destruction of the abrasive grain.

[0003] During the use of microcrystalline sinter abrasive grains, it can be observed in many applications that during the grinding process the abrasive grain, with comparable hardness and density, behaves the more favorably the more delicately the structure is developed. Particularly fine structures may be obtained via sol/gel processes in which e.g. super-finely dispersed aluminum oxide monohydrate of the Boehmite type is used as a base material which – after having been dissolved as a colloid – is processed into a gel which is then further processed into a compact and dense α Al_2O_3 sinter body via a drying, calcination and sintering phase.

Subsequently, it is processed into an abrasive grain. The advantage of the sol/gel method for the production of corundums with microcrystalline structure lies in the fact that reactive base materials with very small components are used and the resulting green bodies can be condensed at relatively low sintering temperatures which favors the formation of a fine structure.

[0004] In EP-B-0 152 768, microcrystalline corundums are described that are produced using the sol/gel technique with the addition of characteristic crystallization seeds at sintering temperatures of approximately 1,400 °C and whose primary crystallites have a diameter that is predominantly, or in their entirety, less than 1 μm .

[0005] Due to the low sintering temperatures and through the addition of crystallization seeds, it is possible to severely restrict crystal growth during the sintering process. Even finer structures, with simultaneous high density and hardness, are described in EP-B-0 408 771. According to EP-B-0 408 771 corundum grains with a median crystallite size of < 0.2 μm are obtained via the sol/gel technique as well, with the addition of particularly fine crystallization seeds while maintaining a special temperature and sintering program in which the temperature range between 900 and 1,100 °C is passed within 90 seconds, the material is brought to a maximum temperature that should not exceed 1,300 °C, with subsequent tight sintering below that maximum temperature in the range between 1,000 and 1,300 °C. The temperature program is selected in such a way that high densification is made possible without exposing the sintering body that is formed or, respectively, its preliminary stage, too long to temperatures that would promote crystal growth.

[0006] If one wishes to obtain a structure of the finest possible crystals, one can also use, in addition to the use of crystallization seeds, sintering additives that hinder the growth of crystals or accelerate the sintering process and thereby indirectly restrict the formation of larger crystals. The influence of individual additives to the sintering process and the crystal growth during the sintering of Al_2O_3 is summarized in the "*Journal of the American Ceramic Society Vol. 39, No. 10, 1956*". Of the numerous patents that describe the use of sintering additives or combinations of sintering additives and crystallization seeds for the production of abrasive grains via the sol/gel route, only a few examples will be described in the following. EP-B-0 024 099 describes the addition of spinels or, respectively, of raw materials that are turned into spinels during the course of the production process. EP-B-0 024 099 describes the use of α Fe_2O_3 crystallization seeds in combination with at least one modified component from the group of oxides of magnesium, zinc, cobalt, nickel, zirconium, hafnium, chromium and/or titanium. EP-B-0 373 765 describes – also in combination with α Fe_2O_3 seeds – yttrium and neodymium compounds in addition to the oxides named above, as additional modifying components. The abrasive grains produced in accordance with the above-named methods have advantages for certain uses as compared to the state of the art.

[0007] The multiplicity of the various Al_2O_3 sintering grains can be explained by the fact that the grinding itself is an extremely multifarious process during which the material that is being processed as well as the processing conditions (pressure [against the material], cooling, and others) can be greatly varied. Thus, the most dissimilar materials (varying types of steel, alloys and metals, plastics, wood, stone, ceramic and many more are processed under the most varying conditions, depending on the objective (surface quality, material abrasion, and others). The demands made on the abrasive grain to be used vary accordingly, meaning that the usability and efficacy of an abrasive grain can not be characterized by factors such as hardness, density, and crystallite structure alone. Other criteria such as chemical inertness, heat conductivity, oxidation and temperature resistance, toughness, and others, play an important role as well, depending on the use.

[0008] Additional variables of the grinding process are bonding and the specification of the abrasive agent which can be further variegated through the use of additives (auxiliary abrasive agents, pore formers, et al.).

[0009] Thus, in the case of abrasive grains produced via the sol/gel route, it was attempted in the past not only to increase the efficacy via the fineness of the crystal structure but also to obtain specific favorable properties for certain uses via dopings. EP-B-0 228 856 describes the addition of yttrium that is added – e.g. in the form of an yttrium salt with an easily volatile anion (nitrate, acetate, et al.) - to the α aluminum monohydrate during the sol/gel process and that reacts with the aluminum oxide to yield yttrium aluminum garnet ($3Y_2O_3 - 5Al_2O_3$). This material shows special advantages in the processing of stainless steel, titanium, nickel alloys, Aluminum and other, hard-to chip alloys, but also with ordinary construction steel. Obviously, the imbedding of garnet crystals provide the abrasive grain with a particular wear resistance for those application which is then reflected in a high abrasion output. In addition to the Y_2O_3 or, respectively, its raw materials, the addition of crystallization seeds and/or other sintering additives is described. In EP-B-0 293 164, the addition of rare earths from the praseodymium, samarium, ytterbium, neodymium, lanthanum, gadolinium, cerium, dysprosium, erbium group and/or combinations of several members from this group is described as well. In this process, the rare earths form hexagonal aluminates with Al_2O_3 which, as imbeddings in the Al_2O_3 matrix, obviously increase the wear resistance of the abrasive grain even more. EP-B-0 368 837 describes abrasive grains whose toughness is increased through the formation of whisker-like crystals that are obtained through the addition of cerium compounds. The sol/gel methods also yields composites that are described in DE-A-196 07 709 and that differ from the aforementioned compounds in that in addition to the Al_2O_3 matrix at least two additional discontinuous structural components are present that differ from each other in the mean particle size by at least a factor of 10. In EP-B-0 4 91 184, composites on the basis of Al_2O_3 are described that feature imbeddings of isometric hard substances that are larger by at least a factor of 10 than the primary crystals that the matrix is constructed of.

[00010] All of the aforementioned processes and materials are based on sol/gel technology that makes it possible – with the simultaneous use of sintering additives – to realize a very fine, preferably submicron crystallite structure. Also, the abrasive grains are often tailor-made and optimized for certain areas of utilization through additional dopings.

[00011] In general, abrasive agents or, respectively, abrasive grains can be simply divided into two large groups. Corundum belongs, besides SiC, to the so-called conventional abrasive agents that have been known for a long time and that are produced, and used, cost-effectively in large

quantities. In addition, recently one has been finding more and more often the so-called super abrasives, such as diamond and cubic boron nitride, whose production costs are a thousand fold to ten thousand fold higher as compared to the production costs of conventional abrasive grains, but that provide an extremely favorable price/performance ratio due to their efficacy, the reduced machine down-time related therewith, and the low consumption of the abrasive agent itself or, respectively, the increase of the per-piece number per time unit and abrasive agent.

[00012] However, the use of super abrasives requires specialized machinery which in turn requires the corresponding investments, and that limits the range of uses for high-performance abrasive agents even more.

[00013] Therefore, one of the main objectives in the development of new abrasive grains is to obtain an abrasive grain that can be used in conventional machines but whose performance level lies between conventional abrasive agents and the super abrasives. This has been achieved, in part, with the aforementioned sol/gel corundums that can be used in many grinding operations at a very favorable price/performance ratio. However, the sol/gel corundums must be grouped closer to the conventional abrasive grain types not only because of their production costs but also because of their performance potential, and therefore they are more suitable to replace the conventional corundum types in grinding operations that do not justify the use of super abrasives.

[NOTE: paragraphs 0014-0017 appear unamended (one noted exception) from the originally-filed translation, but have been moved more appropriately to this Background section]

[00014] The term "nanocomposite", which found entry into ceramics approximately 10 years ago, denotes systems that consist of at least two different solid phases of which at least one phase features particle sizes in the nanometer range.

[00015] $\text{Al}_2\text{O}_3/\text{SiC}$ composites in which SiC particles are built into an Al_2O_3 matrix for reinforcement purposes are described in EP-B-0 311 289 and are provided for use in engine or turbine engineering, e.g. as structural ceramics. In this respect, the diameter of the SiC particles whose share in the composite amounts to between 2 and 10 mol % should be below 0.5 μm while the Al_2O_3 particles should not exceed 5 μm . These materials in which the SiC particles are dispersed in the Al_2O_3 particles are characterized by an extraordinary bending strength and

toughness and can be used as structure ceramic in engine engineering due to their good high-temperature properties.

[00016] Similar $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites that contrast with the known whisker, fiber or platelet-reinforced composite materials through their good high-temperature properties and oxidation resistance are described by Niihara in the *Journal of the Ceramic Society of Japan* 99 [10] 974 – 982 (1991). The influence of small-sized SiC particles on the growth of grains and the sintering behavior of the Al_2O_3 matrix is described by Stearns, Zhao and Harmer in the *Journal of the European Ceramic Society* 10 (1992) 473 – 477. The mechanical properties of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites are examined by Zhao, Stearns, Harmer, Chan, Miller and Cook in the *Journal of the American Ceramic Society* 76 [2] 503 – 510 1993. Nanocomposites produced via the sol/gel route are described by the authors Xu, Nakahira and Niihara in the *Journal of the Ceramic Society of Japan*, 1994, 102, 312 – 315.

[00017] While the places in the literature quoted above mostly refer to composites with SiC portions of > 2 mol %, the mechanical properties of hot-pressed $\text{Al}_2\text{O}_3/\text{SiC}$ composites with low portions of SiC are listed in an article by authors Wilhelm and Wruss in the *cfi/Ber. DGK* 75, 40 – 44 (1998). In addition to the places in the literature quoted above, the $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites have been described in numerous other publications that have been largely summarized in an overview by Sternizke in the *Journal of the European Ceramic Society* 17 (1997) 1061 – 1082. In that article the suspicion is vented, too, that $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites could close the gap between conventional abrasive agents and super abrasives. In contrast to this presumption, however, almost all publications mentioned in that article and the material properties quoted therefrom expressly refer to the use as a structural ceramic. Thus, e.g., the microstructures, thermodynamic stability, density, hardness, breaking strength, fracture toughness, the wear behavior and the creep rate are all mentioned. All those values are certain to play a role in the grinding process as well, however without allowing, by themselves, a valid statement about the suitability of any material as an abrasive grain. For example, great hardness is certainly a basic requirement for a material to be used as an abrasive grain. However, as the example of B_4C shows that is often quoted in expert circles and that has never found widespread use as an abrasive grain in spite of its great hardness due to its insufficient chemical and thermal constancy and its high brittleness, a sum of properties must be considered in order to recognize the suitability as an abrasive agent. Other hard substances that range in their hardness values

between conventional abrasives and super abrasives also could not succeed as abrasive grains because they lack additional properties such as toughness, thermal and chemical stability or other prerequisites important for the grinding process. Thus, the nanocomposite materials described in the literature that may have certain properties required for the grinding process, so far have not been able to be successfully used as abrasive grains. They rather behave similarly to those cutting ceramics on Al_2O_3 basis that have been used with great success e.g. in milling or lathing but that – processed for graining – in grinding show only an unsatisfactory abrasion performance that lies on the level of conventional melting corundums or even below that.

Summary of the Invention

[00018] Therefore, an objective of the present ~~the task of the invention at hand~~ is to make available abrasive grains with an even better performance potential - as compared with the aforementioned state of the art – as well as a process for their production. In accordance with the invention, this objective is achieved through a method for the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains, in which an aluminum-oxide containing sol is mixed with sinter additives and SiC nanoparticles and subsequently gelled, dried, calcined and sintered, wherein the sintering is conducted by heating the mixture in the range between 1300°C and 1600°C. The process yields sintered $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains having hardness greater than 16 GPa, densities greater than 95% of the theoretical limit, and an SiC portion of between 0.1 and < 5 mol %, relative to the Al_2O_3 matrix, wherein the SiC particles are present in the Al_2O_3 matrix as well as intra-granularly and the abrasive grain shows a performance factor $\text{LF}_{25} > 75$ % in the single-grain scratch test. ~~task is solved through the characteristics of Claim 11 or, respectively, of Claim 1.~~

[00019] ~~The sub-claims concern advantageous models of the invention.~~ In certain embodiments, the aluminum-oxide containing sol contains as a solid component superfinely dispersed aluminum oxide monohydrate of the Boehmite type, aluminum alkoxides, aluminum halogenides and/or aluminum nitrate. The SiC nanoparticles may be added in an amount of between 0.1 and < 5 mol %, preferably in the range of 0.3 and 2.5 mol % relative to the aluminum contents of the mixture, calculated as Al_2O_3 . Prior to the gelling, sintering additives may be added in the form of crystallization seeds, crystal growth inhibitors and/or other

modifying components that influence the sintering process. Fine-particled α aluminum oxide may be used as crystallization seed.

[00020] The gelling of the suspensions is controlled by increasing or decreasing the pH value, through aging, the addition of electrolytes, increased temperature, and/or concentrating the solution. The gel drying is preferably accomplished in a temperature range between 50°C and 120°C, with subsequent calcination between 500°C and 800°C, and sintering in a temperature range between 1300°C and 1600°C (preferably between 1380°C and 1500°C and under inert conditions.) Communion to the desired grain size may be performed before or after sintering.

[00021] The SiC portion of the nanocomposite abrasive grain preferably amounts to between 0.3 and < 2.5 mol %, relative to the Al_2O_3 matrix, and are predominantly present intragranularly in the Al_2O_3 matrix. The Al_2O_3 crystals of the matrix exhibit mean diameters of between 0.2 μm and 20 μm , and are typically formed in the submicron Al_2O_3 matrix. The Al_2O_3 matrix has a submicron structure and a mean particle size of < 1 μm , preferably < 0.5 μm . The coarse Al_2O_3 crystals have a mean diameter of > 2 μm , preferably > 5 μm , and exhibit an oblong shape. The coarse Al_2O_3 crystals have a length/width ratio of between 2:1 and 10:1, preferably between 4:1 and 6:1.

[00022] ~~Claim 20 concerns a suitable utilization of the abrasive grains obtained in accordance with the invention.~~ $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains in accordance with the invention, when utilized with backing substrates or materials, are useful in grinding belts or grinding disks.

Brief Description of the Drawing

[00023] A detailed description of preferred embodiments of the present invention are provided below with reference to the figures of the drawing, in which:

[00024] Figure 1 is an elementary illustration of a test stand for one-grain scratching;

[00025] Figure 2 is a chart illustrating a comparison of abrasion curves for nanocomposite grains per the present invention to those of prior art abrasive grains;

[00026] Figure 3 is a microphotograph of a matrix with coarse crystalline imbeddings; and

[00027] Figure 4 is another microphotograph of a matrix with coarse crystalline imbeddings.

Detailed Description of Preferred Embodiments of the Invention

[00028] Now, in practice, it has turned out to be extremely difficult to characterize the usability or, respectively, the abrasive behavior to be expected of an abrasive grain solely on the basis of certain material properties of which one knows that they have – each considered by itself – a positive effect on the grinding behavior. So far, theories about the mechanisms that actually occur during the abrasion of matter by an abrasive could only be developed after the process by way of the processed work piece and based on the changes of the grinding tool. In addition to all material properties of the abrasive grain, the condition of the grinding tool (bonding, porosity, additives et al.), of course, and the work piece itself have an influence on the grinding behavior which makes it often difficult, even after the fact, to draw a correlation between the grinding result and certain material properties of the abrasive grain. A final statement can be obtained only through process-engineering tests of abrasive agents or even only through practical or field tests that are connected with considerable expenditures of money and time.

[00029] Therefore it is worth trying to find an independent measuring method and measuring magnitude that permit a direct statement about the suitability of a material as an abrasive grain. In practice, the so-called single-grain test (illustration of a test apparatus shown in Figure 1~~Illustration 1: single-grain scratch test~~) has proved more and more successful in recent years, in which a single abrasive grain is examined under conditions as realistic as possible, simulated after the grinding process. The test device is a retooled surface grinding machine on which a scratch disk is mounted on the grinding spindle in lieu of the grinding disk. The scratch disk that is made, for practical reasons, of a relatively light and easy-to-work material (e.g. aluminum) features on its circumference a holding device with an abrasive grain soldered onto it. During the scratching phase itself the supporting table with the work piece attached to it moves in direction x against the rotation direction under the rotating scratching disk. Because of a pre-set feed motion in direction y, the abrasive grain that protrudes beyond the circumference of the disk generates with each revolution a scratch trace in the work piece. With increasing scratch length or, respectively, scratching time, the scratch depth and the scratch cross section decrease due to grain wear until the grain tip has been worn off by the feed motion amount in direction y and no longer leaves a trace. The scratch traces can be scanned with a surface measuring device and then be evaluated. The measuring principle is shown in Figures 1 and 2~~Illustrations 1 and 2~~ and will be explained in the following by means of the reference numbers.

[00030] **Figure 1** ~~Illustration 1~~ shows the theoretical design of the test stand with the scratching disk (1) and the scratching grain (2), the movable axles (3, 4, 5) in directions x, y, and z, the work piece (6), the support table (7) and the grinding spindle head (8). For the measuring itself, standard conditions must be defined for the cutting speed v_c , the work piece speed v_w , and the feed motion a_e , that are preferably adapted to the grinding operation for which one wishes to use the abrasive grain later. In addition, the work piece material and the use of a cooling lubricant (9) must be determined.

[00031] The evaluation principle can be seen in the curves for various abrasive grain types shown as examples (**Fig. 2** ~~III. 2~~) in which the scratch cross section A_{Rn}/A_{R0} is outlined against the scratch length I_R . In this context, A_{R0} is the scratch cross section after the first intervention, and A_{Rn} the scratch cross section after n mm of scratch length.

[00032] The performance factor LF_{25} for the single grain results from the intersection of the characteristic curve for the individual grain type with the ordinate after a scratch length of 25 mm and corresponds to the change of the scratch cross section A_{Rn}/A_{25} . The performance factor is expressed in % relative to the theoretical case that no abrasion of the grain occurs and $A_{R25} = A_{R0}$. The evaluation after a scratch length of 25 mm was chosen because in the typical course of the curve the decisive first and steep section of the curve during which the grain is under the most stress has been concluded. This section which also comes relatively close to the actual grinding process with regard to the feed motion permits a very good statement about the performance potential of an abrasive grain. In the further course, the curves flatten since the grains are now stressed less due to the reduction in the feed motion and thus wear off less rapidly. In order to obtain a representative result for a grinding granulation, at least 20 grains of a grain type should be measured and the abrasion curve should be formed from the mean values of the individual measuring points.

[00033] The single-grain scratch test thus permits – quite consistently with the results obtained in practice – to evaluate the suitability of an abrasive grain in which all values relevant for the grinding process, such as hardness, toughness, density, resistance, creeping speed, thermal and chemical resistance, crystallite structure, et al., flow indirectly into the total, without certain properties or, respectively, certain property combinations, having to be explicitly known or recognized and needing to be taken into account. For all properties, however, certain minimum requirements must be met for a material to be considered as an abrasive grain. Thus,

e.g., a material whose hardness is clearly below the usual hardness for abrasive agents would never be suitable for grinding even if all other properties were outstanding.

[00034] Surprisingly, for $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites with SiC portions under 5 mol % that were produced via a direct sol/gel route with the addition of crystallization seeds, performance factors were found in accordance with the method described above that are clearly above the performance factors found thus far in the case of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. The performance factors of the nanocomposites according the invention are also above the values of the known pure or doped sol/gel corundums and thus between the conventional abrasive grains and the super abrasives in the target area.

[00035] In contrast with the known $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites that are produced by blending the basic substances and subsequent condensing (e.g. through hot pressing, pressure-less sintering or hot isostatic pressing) and sintering, the production of the abrasive grains according to the invention proceeds in hydrochemical fashion via a direct sol/gel route with the use of crystallization seeds. Xu, Nakahira and Niihara describe in their article in the *Journal of the Ceramic Society of Japan*, 1994, 102, 312 – 315 the use of the sol/gel technology in the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites. However, they use the technology only in order to achieve the most homogeneous possible blend of the nano powders via an upstream colloidal solution of the particles. The sol is subsequently processed, through drying and calcination, into a homogeneous blend of ultra fine Al_2O_3 and SiC powders that are then hot-pressed – in analogy with conventional powder technology – under nitrogen at a pressure of 30 MPa and a temperature of 1,600 °C.

[00036] Due to the isolation of the powder as an interim product and subsequent conventional processing in terms of powder engineering, certain advantages of the sol/gel method that are important for the production of an abrasive grain are lost. The properties in terms of grinding engineering of a composite produced via the above-mentioned method therefore correspond to those of the aforementioned nanocomposite. In addition, there are economic aspects because cost-effective mass production on an industrial scale can not be realized via a hot-pressing method.

[00037] In the direct sol/gel method according to the invention for the production of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites, on the other hand, an Al_2O_3 sol is first produced in the usual manner. As solid components for the aluminum oxide containing sol, micro-dispersed aluminum oxide

monohydrate of the Boehmite type, aluminum alkoxides, aluminum halogenides and/or aluminum nitrate are suitable that are dispersed with the aid of a disperser, a strong stirrer, or through the use of ultrasound. The solid contents of the suspension preferably lies between 5 and 60 weight %. Nanoscaled SiC is then added to this suspension, likewise preferably in the form a suspension in order to achieve the most homogeneous possible distribution, between 0.1 and < 5 mol %, preferably in the area of 0.3 and 2.5 mol % relative to the aluminum contents of the mixture calculated as $\text{Al}_2\text{O}_3/\text{SiC}$. It is of course possible, too, to stir SiC as a solid into the described suspension. As the examples in Table 3 show, especially good results are obtained with comparatively small amounts of SiC. As an SiC basis, most finely ground SiC powder obtained via the Acheson process, or nanopowders produced through thermal or laser-supported gas phase reactions or various plasma methods, are suitable.

[00038] In order to favorably influence the later sintering process sintering additives in the form of crystallization seeds, crystallization growth inhibitors and/or other modifying components may be added prior to gelling. For this purpose, all known sintering additives for Al_2O_3 are suitable, e.g. the spinel-forming oxides of Co, Mg, Ni, and Zn, the oxides of Ce, Cu, B, Ba, Hf, K, Li, Nb, Si, Sr, Ti, Y, Zr, or the rare earths or, respectively, their precursors, and the oxides with corundum-like structure such as Fe_2O_3 , Cr_2O_3 , Al_2O_3 , or others that act as crystallization seeds. In order to obtain certain properties of the abrasive grain, combinations of the above may, of course, be used as well.

[00039] Preferably, the Al_2O_3 sol is treated with an aqueous suspension of super-finely ground $\alpha\text{-Al}_2\text{O}_3$ particles prior to the addition of SiC. The maximum particle size of the $\alpha\text{-Al}_2\text{O}_3$ particles that serve as crystallization seeds is below μm , preferably below 0.2 μm . The amount of seed material to be used depends on the particle size and lies between 0.5 and 10 weight % relative to the Al_2O_3 contents of the end product. Since it depends on the number of seeds, in addition to the fineness, even very small weight amounts of superfine seeds will suffice to promote the sintering process.

[00040] The prepared suspension is then heated to the boiling point and expediently gelled through the addition of acid. Here, too, it is possible again to apply as an alternative any other type of gelling (aging, addition of electrolyte, temperature increase, concentration of the suspension, at al.). Drying of the gel (after cooling off) is carried out within a temperature range between 50 °C and 120 °C. Subsequently, calcination occurs in a temperature range between

500 °C and 800 °C in order to evaporate the residual water and the acid. After calcination, the composites are present as green bodies with diameters of up to several millimeters, and are then sintered. The advantage of direct compression lie particularly in the high sintering activity of the dried and calcinated green bodies in which the original materials are already bound to each other chemically, with the compression and solidification to the finished composite thus proceeding considerably more effectively and favorably.

[00041] This process and thus the product quality may be further improved through the additional use of sintering additives or, respectively, crystallization seeds. The sintering of the calcined gel preferably occurs at temperatures between 1,300 °C and 1,600 °C, preferably under inert conditions (e.g. a nitrogen atmosphere), and particularly advantageously in a gas-tight rotary oven in order to realize the fastest possible heating of the product and a short sintering time which has a particularly favorable effect on the structure and thus on the efficacy of the abrasive grain. Alternatively, any other known oven type may be used that allows fast heating rates and high temperatures. Since the sintering occurs very fast, processing it is even possible in a vacuum or in an oxidizing atmosphere since the largest portion of the SiC nanoparticles are imbedded in the matrix and are thus protected from oxidation.

[00042] Comminution to the desired granulation may occur before or after sintering with the usual comminution aggregates. Preparing the calcinated gel in its green state is advantageous since after sintering considerably more energy must be expended on comminution of the then dense and hard composite material.

[00043] During sintering, the nanoscaled SiC acts as crystal growth inhibitor for the Al₂O₃ matrix, but at the same time delays the condensing of the green body, making it necessary to use comparatively – as compared with a sol/gel material on pure aluminum oxide basis - high sintering temperatures in order to achieve sufficient condensation of the material during which step not inconsiderable crystal growth may occur. For example, large crystals occur already at approximately 1,400 °C in larger numbers. This phenomenon has already been described in US patent 4,623,364. The undesirable occurrence of coarse crystals in an otherwise fine matrix was attributed to impurities. There, the objective is to obtain a fine-crystalline matrix with as few coarse parts as possible as it is disclosed in the initially quoted patents and as it corresponds to the state of the art.

[00044] Surprisingly, it was then found that the abrasion output of the nanocomposite abrasive grain according to the invention is particularly high when a certain portion of coarse crystals with lengths of up to 20 μm and a mean diameter of $> 2 \mu\text{m}$, preferably $> 5 \mu\text{m}$, is present in the matrix. The abrasion output lies clearly above that of the finely structured pure sol/gel Al_2O_3 abrasive grains whose mean crystallite size is commonly 0.2 – 0.3 μm and in which all crystals are present in the sub micron range, preferably in the range below 0.4 μm . This is all the more surprising since in expert circles it has generally been known that the abrasion output of sinter corundums with increasingly fine structure - particularly in the d_{50} range under 0.5 μm – increases drastically.

[00045] As examples 1 – 6 and comparison examples 7 – 11 which describe the influence of sinter conditions on the structure and the efficacy of sinter corundum show, the output curve of the $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite follows a non-linear course with a maximum at a sintering temperature between 1,400 °C – 1,450 °C. The first coarsely crystalline and columnar crystals occur in the matrix within this temperature range with a holding time of 30 minutes. The coarse Al_2O_3 crystals preferably have an oblong shape, with a length/width ratio of between 2:1 and 10:1, particularly preferably between 4:1 and 6:1. Typical images of the matrix with coarse-crystalline imbeddings are reproduced as electron-microscopic photos in **Figures 3 and 4** ~~Illustrations 3 and 4 on page 19~~. Below 1,400 °C, a purely submicron structure occurs, with all particles being present in the range of $< 1 \mu\text{m}$, preferably $< 0.5 \mu\text{m}$. The output potential of these materials lies also above that of pure state-of-the-art sol/gel corundums, but surprisingly below the materials with coarse-crystalline imbeddings obtained in the abovementioned temperature range. The output curve goes down again at still higher temperatures which bring about an increased occurrence of coarse crystals.

[00046] However, even at sintering temperatures of 1,500 °C with high portions of coarse crystals, grinding performances are achieved that are on the level of the best pure sol/gel corundums. In contrast, with the pure sol/gel corundums an almost linear course of the output potential can be discerned in accordance with the fineness of the structure, and only in the submicron range, at a mean crystallite size d_{50} of $< 0.4 \mu\text{m}$, are good performances achieved.

[00047] Obviously, the coarse crystallites in the nanocomposites cause some kind of structural strengthening that has a positive effect on the wear behavior of the grain and compensates not only for the expected performance decrease caused by grain growth but also provides the

abrasive grain, in combination with the imbedded SiC nanoparticles, with a clear performance increase.

[00048] By way of the examples in Table 4 it can be seen that the product improvement through the imbedding of SiC particles is limited not only to SiC nanopowder, but also that outstanding abrasive performances can be achieved with grains that show relatively coarse SiC embeddings. However, it is clear that the trend is unambiguous that the abrasive performance is the better for the finer the SiC powders are. Initially, for commercial reasons and for reasons of availability, in the production of the abrasive grain according to the invention, the powders listed in the examples that were obtained through extremely fine grinding of industrial SiC produced via the Acheson method were used exclusively~~[this sentence is ungrammatical and/or incomplete in the German original]~~. However, one may assume that the abovementioned trend will continue when even finer powders are being used.

[00049] The SiC particles in the case of the nanocomposites according to the invention may be arranged intra-granularly – in the Al_2O_3 matrix particles – as well as inter-granularly – at the grain borders between the Al_2O_3 particles - and it can be observed that the smaller particles are preferably integrated in intragranular fashion. The question of what influence the type of imbedding of the SiC particles has on the abrasive performance is the subject of extensive reviews and can at present be contemplated only speculatively.

[00050] Some theories are discussed in the afore-quoted publications which, however, again refer exclusively to individual properties of composite materials and which do not take into account the effect of the sum of properties that is decisive for abrasive performance. However, examples 14 – 17 clearly show the trend that abrasive performance increases with a decrease of the particle size of the embeddings. This allows the conclusion that, above all, intragranularly imbedded SiC is responsible for the improvement of abrasive performance.

[00051] Therefore, the invention creates a nanocomposite abrasive grain on Al_2O_3 basis with predominantly intragranularly imbedded SiC nanoparticles that shows a hardness ($\text{HV}_{0.2}$) of greater [than] 18 GPa, whose density is above 95% of the theoretical density, and that has a performance factor LF_{25}^* of $> 75\%$ (* = measured as the mean value of 20 individual measurings on the material 100Cr6 ($\text{HRC} = 62$) with a cutting speed of 30 m/s, a feed motion of 20 μm , a work-piece speed of 0.5 mm/s, and with the use of a 3% emulsion as coolant).

[00052] In the following, the invention will be explained by way of examples; this does not constitute any limitation of the invention.

[00053] **Examples 1 – 6**

[00054] **Suspension A (Boehmite Sol)**

[00055] 10 kg of pseudo-boehmite (Disperal, firm of Condea) are dispersed with the use of a dispergator (type Megatron MT 1-90, firm of Kinematica) in 50 ml of distilled water whose pH value was adjusted to 2.4. Approximately 300 ml of a 50% α Al_2O_3 -containing Keim-Slurry with a maximum particle size of $d_{\text{max}} = 0.4 \mu\text{m}$ that was obtained through wet-grinding and subsequent centrifugation of a fine-particled α - Al_2O_3 powder (CS400M, firm of Martinswerk) is added, again with the use of a dispergator. Following the addition of the Keim-Slurry, there are approximately 2 weight % of Al_2O_3 crystallization seeds in the sol.

[00056] **Suspension B (SiC Suspension)**

[00057] 1.5 g of a 50% aqueous polyethylene imine suspension (firm of Fuka) is added to 600 ml distilled water, stirring vigorously. Subsequently, 30 g of nanoscaled SiC (UF 45, firm of H.C. Starck) is stirred into the diluted suspension.

[00058] Suspension B is added to the Boehmite/sol suspension (Suspension A) while stirring, and the pH value of the mixture is adjusted to 1.8 with the aid of nitric acid. Subsequently, the mixture is heated to 95 °C, stirring constantly, and gelling is initiated by adding additional nitric acid drop by drop. After cooling off, the gel is dried at 85 °C in the drying chamber. The dried gel is pre-crushed to a particle size of less than 5 mm and then calcined at approximately 500 °C.

[00059] In examples 1 –6, only the sintering temperatures were varied. In Table 1, the measured hardness values, performance factors and crystallite structures are listed as a function of the sintering conditions.

[00060] **Table 1: Examples 1 – 6**

Example	Sintering Program*	Hardness (HV _{0.2})	Crystallite Structure (d ₅₀)	LF ₂₅ %
1	1300 / N ₂ / 60 / 30	11.3 GPa	< 0.4 μm	23
2	1350 / N ₂ / 60 / 30	13.3 GPa	< 0.4 μm	29
3	1380 / N ₂ / 60 / 30	19.8 GPa	< 0.4 μm	73

4	1400 / N ₂ / 60 / 30	22.9 GPa	1 μm	85
5	1450 / N ₂ / 60 / 30	20.7 GPa	5 - 10 μm	83
6	1500 / N ₂ / 60 / 30	20.1 GPa	10 - 20 μm	70

* Sintering Program = sintering temperature (°C) / oven atmosphere / heating rate (°C/min) / holding time (min)

[00061] Comparison Examples 7 – 11 (without SiC Embeddings)

[00062] 10 kg of pseudo-Boehmite (Disperal, firm of Condea) are dispersed with the use of a dispergator (type Megatron MT 1-90, firm of Kinematica) in 50 ml of distilled water whose pH value was adjusted to 2.4. Approximately 300 ml of a 50% α Al₂O₃-containing Keim-Slurry with a maximum particle size of $d_{\text{max}} = 0.4 \mu\text{m}$ that was obtained through wet-grinding and subsequent centrifugation of a fine-particle α Al₂O₃ powder (CS400M, firm of Martinswerk) is added, again with the use of a dispergator. Following the addition of the Keim-Slurry, there are approximately 2 weight % of Al₂O₃ crystallization seeds in the sol.

[00063] The pH value of the mixture is adjusted to 1.8 with the aid of nitric acid. Subsequently, the mixture is heated to 95 °C, stirring constantly, and gelling is initiated by adding additional nitric acid drop by drop. After cooling off, the gel is dried at 85 °C in the drying chamber. The dried gel is pre-crushed to a particle size of less than 5 mm and then calcined at approximately 500 °C.

[00064] In comparison examples 7 - 11, too, only the sintering temperatures were varied. Table 2 shows the measured hardness values, performance factors and crystallite structures as a function of the sintering conditions.

[00065] Table 2: Examples 1 – 6

Example	Sintering Program*	Hardness (HV0.2)	Crystallite Structure (d50)	LF25%
7	1240 / N ₂ / 60 / 30	19.7 GPa	0.2 – 0.3 μm	75
8	1300 / N ₂ / 60 / 30	22.4 GPa	1 μm	63
9	1350 / N ₂ / 60 / 30	23.1 GPa	1 - 5 μm	60
10	1400 / N ₂ / 60 / 30	21.6 GPa	3 - 7 μm	49
11	1450 / N ₂ / 60 / 30	20.6 GPa	5 - 10 μm	40

* Sintering Program = sintering temperature (°C) / oven atmosphere / heating rate (°C/min) / holding time (min)

[00066] Example 12

[00067] The production of Example 12 occurs analogously to Examples 1 – 6. However, 75 g of nanoscaled SiC UF45 were utilized.

[00068] Example 13

[00069] Production occurred analogously to Example 12. Instead of 75 g, 150 g nanoscaled SiC UF45 were used. Table 3 shows the performance factors as a function of SiC concentration.

[00070] Table 3: Examples 4, 12, and 13

Example	Sintering Program	Hardness (HV0.2)	SiC Portion (mol %)	LF25 (%)
4	1400 / N2 / 60 / 30	22.9 GPa	1.0	85
12	1400 / N2 / 60 / 30	22.4 GPa	2.5	59
13	1400 / N2 / 60 / 30	23.1 GPa	5.0	37

[00071] Example 14

[00072] Production of Example 14 occurred analogously to Example 4. Instead of SiC UF45, the somewhat coarser SiC UF25 (firm of H.C. Starck) was used. Sintering was done at a temperature of 1400 °C in a nitrogen atmosphere. The heating rate was 60 °C per minute, and the holding time was at 30 minutes.

[00073] Example 15

[00074] Production of Example 15 occurred analogously to Example 14. Instead of SiC UF25, the coarser SiC UF15 (firm of H.C. Starck) was used.

[00075] Comparison Example 16

[00076] Production of Example 16 occurred analogously to Example 15. Instead of SiC UF15, an SiC P1000 (firm of Elektroschmelzwerk Kempten) was used.

[00077] Comparison Example 17

[00078] Production of Example 17 occurred analogously to Example 16. Instead of SiC P1000, an SiC P600 (firm of Elektroschmelzwerk Kempten) was used.

[00079] Table 4 shows the performance factor of the nanocomposite as a function of the particle size of the embedded SiC's.

[00080] **Table 4: Examples 4, 15 – 18**

Example	SiC	Mean Particle Size d50	Hardness (HV0.2)	LF25 (%)
4	UF45	300 nm	19.7 GPa	85
14	UF25	500 nm	22.4 GPa	82
15	UF15	600 nm	23.1 GPa	77
16	P1000	18 μ m	21.6 GPa	73
17	P600	26 μ m	23.3 GPa	58

[00081] **Abrasion Tests**

[00082] In addition to the scratching test, a few selected examples were subjected to an abrasion test on an abrasive belt. The results of the tests are summarized in Table 5.

Table 5: Abrasion Tests (Belt Grinders)

Abrasive Grain	Type of Steel			
	Turbine Steel		Titanium Alloy	
	Abrasion (g)	Output (%)	Abrasion (g)	Output (%)
Example 4	1096	145	127	176
Example 5	994	131	109	151
Example 14	1023	135	112	155
Example 15	843	111	85	118
Example 7	781	103	68	94
commercial sol/gel corundum	757	100	72	100
melt corundum	320	42	23	32

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Illustrations

[see original drawing]

~~III. 1: Elementary diagram of the test stand for one grain scratching~~

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<u>Grinding Conditions:</u>		
rel. scratch cross section		
A_{R0}/A_{R0}	Material:	100Cr6
	Cutting speed v_c :	30m/s
	Feed motion a_a :	20 μ m
[see original]	Work piece speed v_w :	0.5 mm/s
	Coolant:	3% emulsion
	cBN	
	Example 4	
	sol/gel corundum	
	melt corundum	
	structure ceramics	
	(Al ₂ O ₃ /5%SiC)	
	mm scratch length	

III. 2: Abrasion curves of Al₂O₃/SiC nanocomposites as compared with some typical abrasive grains

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~~[photograph]~~

~~Figure 3~~

~~[photograph]~~

~~Figure 4~~

Abstract of the Disclosure

The invention relates to a method for producing $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains. SiC nanoparticles are added to a sol containing aluminum oxide and said sol is then gelatinized, dried, calcinated and sintered. The invention also relates to $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite abrasive grains.

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